

Table 3. Fractional coordinates and thermal parameters

The thermal expression is of the form:

$$T = \exp [-\frac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)].$$

Nonhydrogen atoms

Positional parameters are multiplied by 10⁵.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> ₁₁	<i>B</i> ₂₂	<i>B</i> ₃₃	<i>B</i> ₁₂	<i>B</i> ₁₃	<i>B</i> ₂₃
O	48680 (10)	62746 (22)	16107 (9)	2·41 (6)	2·76 (6)	4·17 (7)	0·30 (4)	1·05 (5)	1·19 (4)
N(1)	36640 (13)	28911 (25)	15637 (10)	2·12 (6)	2·88 (7)	2·92 (7)	-0·05 (4)	0·56 (5)	-0·23 (5)
N(2)	61009 (13)	28897 (24)	18802 (11)	2·25 (7)	2·85 (7)	3·17 (7)	0·23 (4)	1·10 (5)	-0·11 (5)
C(1)	42756 (14)	16284 (28)	24073 (12)	2·21 (8)	2·11 (7)	3·53 (8)	-0·37 (5)	0·84 (6)	-0·03 (5)
C(2)	38290 (15)	52334 (29)	18244 (13)	1·98 (7)	2·59 (8)	3·87 (9)	0·25 (5)	0·80 (5)	0·42 (6)
C(3)	60165 (15)	52382 (29)	21092 (13)	2·06 (7)	2·62 (8)	3·87 (9)	-0·07 (5)	1·06 (6)	0·36 (6)
C(4)	40375 (18)	22260 (41)	7322 (14)	3·15 (9)	5·34 (11)	3·18 (9)	-0·19 (7)	0·69 (6)	-1·06 (7)
C(5)	54654 (18)	22221 (42)	9207 (15)	3·31 (9)	5·07 (11)	3·50 (9)	0·39 (7)	1·37 (7)	-0·85 (8)

Table 3 (cont.)

Hydrogen atoms

Positional parameters are multiplied by 10⁴.

	<i>x</i>	<i>y</i>	<i>z</i>
H(1)	3674 (28)	684 (57)	539 (22)
H(2)	3653 (28)	3424 (59)	173 (22)
H(3)	3920 (23)	148 (48)	2378 (18)
H(4)	3169 (26)	6216 (45)	1458 (20)
H(5)	3359 (27)	6226 (45)	3093 (21)
H(6)	4254 (28)	879 (58)	4176 (22)
H(7)	4378 (28)	3218 (56)	4551 (24)

(The hydrogen atoms were assigned thermal parameters equal to those of the adjoining heavier atom.)

and showed that this treatment compared favorably with various explicit correction schemes. Refinement of the abbreviated data set led to an *R* of 0·053 for this compound; recalculation of the *R* value for the full data set (including the reflections with secondary extinction errors) gave a value of 0·098. All of the *R* values quoted above are based on calculations which include the 'unobserved' (zero intensity) reflections. The observed and final calculated structure factors are listed in Table 2.

Full-matrix least-squares methods were used at all stages of the refinement; the function minimized was $\sum w(F_o - F_c)^2$. Each reflection intensity was initially given a weight of unity, and this was not changed until all hydrogen atoms were found. At this later stage, a statistical examination of the remaining discrepancies suggested the weighting function: $1/w = 1.0 + [(|F_o| - 4)/8]^2$, which gives a distribution of weights consistent with the distribution of errors expected in counter diffractometry. The positions of the hydrogen atoms were varied during the weighted refinement, and all converged satisfactorily. Each hydrogen atom was assigned a thermal parameter equal to that found for its neighboring heavier atom in the previous refinement cycle. The refined atomic parameters are given in Table 3.

Discussion of structure

The cage structure (Fig. 1) can be viewed as two layers of boat-shaped six-membered rings. The lower layer

consists of two fused piperazine rings; the upper layer is a dioxane ring. The 'sides' of this cage are five-membered rings [Fig. 1(b)] in the envelope conformation, and the ends are seven-membered rings which could also be described as boat-shaped.

The carbon-carbon bond which forms the junction of the piperazine rings [C(1)-C(1')] is the only bond which appears to be significantly lengthened by cage formation (Fig. 2); its length is 1.574 ± 0.003 Å rather than the expected 1·53-1·55 Å value. There are two pairs of eclipsed bonds interacting across this particular C-C bond. This amount of lengthening is not unusual; a similar formation of eclipsed bonds about a C-C bond was observed, for example, by Schwarzenbach (1968) in the structure of a cage compound. The bond length reported there was also 1.574 ± 0.008 Å.

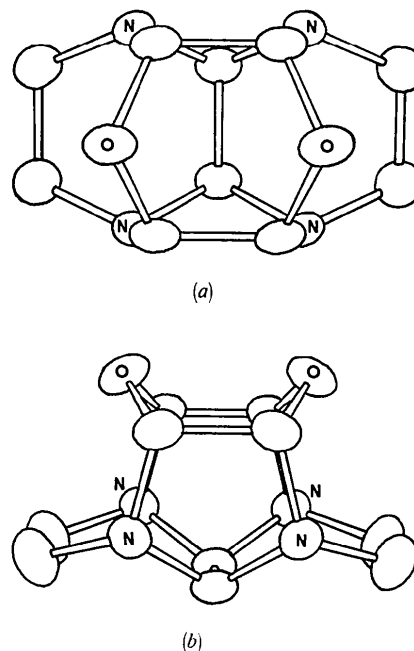


Fig. 1. Two views of the cage skeleton: (a) projected down the crystallographic twofold axis, and (b) rotated 90° from the first view about the long axis of the molecule.

unusually tight packing. The packing is illustrated in Fig. 3. There are no opportunities for hydrogen bonding and no overall dipolar attractions. There are only a few intermolecular distances less than 3.6 Å (Fig. 3). However, each atom interacts with several atoms from neighboring molecules at distances only slightly longer (3.6 to 3.8 Å). The molecules mesh together neatly, accounting for the relatively high density.

References

- EDWARDS, J. M., WEISS, U., GILARDI, R. D. & KARLE, I. L. (1968). *Chem. Commun.* p. 1649.
 HAUPTMAN, H. & KARLE, J. (1959). *Acta Cryst.* **12**, 553.
 KARLE, J. & HAUPTMAN, H. (1956). *Acta Cryst.* **9**, 635.
 KARLE, J. & KARLE, I. L. (1966). *Acta Cryst.* **21**, 849.
 SCHWARZENBACH, D. (1968). *Acta Cryst.* **B24**, 238.
 ÅSRINK, S. & WERNER, P.-E. (1966). *Acta Cryst.* **20**, 407.

Acta Cryst. (1972). **B28**, 746

The Crystal Structure of Ammonium Oxalate Monoperhydrate

BY BERIT F. PEDERSEN

Sentralinstitutt for industriell forskning, Oslo 3, Norway

(Received 21 May 1971 and in revised form 2 August 1971)

The crystal structure of ammonium oxalate monoperhydrate $(NH_4)_2C_2O_4 \cdot H_2O_2$, has been determined from three-dimensional X-ray diffractometer data. The compound crystallizes in the orthorhombic space group $P2_12_12$, with two molecules per unit cell. 6% of the H_2O_2 molecules are found to be exchanged with H_2O molecules occupying randomly distributed sites. Both the oxalate ion and the hydrogen peroxide molecule are situated on twofold axes. The interatomic dimensions of the oxalate ion are normal, but the ion is *non-planar*. The planes of the two C–C–O₂-groups of the ion are inclined at an angle of 28.15 (9)°. The hydrogen peroxide molecule has a skew conformation with a dihedral angle of 121 (3)°, the acceptor angle being 127.77 (9)°. The interatomic dimensions are of normal values. All available hydrogen atoms are engaged in hydrogen bonds; O–H...O is 2.625 (1) Å and the N–H...O average distance is 2.860 (1) Å. Single crystals of the perhydrate transform to single crystals of the hydrate over a period of several months. No variation in unit-cell dimensions is found for different batches of crystals, and no gradual variation in unit-cell dimensions seems to accompany the transformation from the perhydrate to the hydrate.

Introduction

Investigations are being carried out at this institute to study the structure and bonding of the hydrogen peroxide molecule in solids (Pedersen, 1969a). Previously it has been found that the hydrogen peroxide molecule forms stoichiometric compounds with all the alkali metal oxalates. The crystal structures of the following compounds have been determined: $Li_2C_2O_4 \cdot H_2O_2$ (Pedersen, 1969b), $Na_2C_2O_4 \cdot H_2O_2$ (Pedersen & Pedersen, 1964), $K_2C_2O_4 \cdot H_2O_2$ and $Rb_2C_2O_4 \cdot H_2O_2$ (Pedersen, 1967). Evidence has been found that caesium oxalate also forms a perhydrate. In this paper the crystal structure of ammonium oxalate monoperhydrate will be described in detail. A preliminary note (Pedersen, 1969c) has been published, but as indications of non-stoichiometry were found in this compound, a detailed discussion was postponed until more accurate intensity data were available.

The crystal structure of ammonium oxalate monoperhydrate is closely related to the structure of ammonium oxalate monohydrate (Robertson, 1965). A similar analogy has been observed previously for the potassium and rubidium oxalates, which also form

both monohydrates and monoperhydrates (Pedersen, 1967). The crystal structure of ammonium oxalate monohydrate, which has previously been carefully refined from three-dimensional X-ray data at 30°K (Robertson, 1965), shows all available hydrogen atoms to be engaged in hydrogen bonds and the oxalate ion to be *non-planar*, the dihedral angle between the two C–C–O₂ planes being 26.6 (4)°. The non-planarity is believed to be caused by the hydrogen bonding network.

By substituting the water molecule by a molecule of hydrogen peroxide, one would expect changes in the crystal structure. Slight changes in packing and hydrogen bonding possibilities may lead to changes in the unusual twisted conformation of the oxalate ion, which hitherto has been observed only for the hydrogen oxalate ion (Haas, 1964; Pedersen, 1968; Follner, 1970; Tellgren & Olovsson, 1971).

The hydrogen peroxide molecule in the gas phase has a dihedral angle of 111.5°. The molecule has, however, been found to show great variation in dihedral angle, from 90 to 180°, in the solids that so far have been studied in detail. As ammonium oxalate contains only light atoms, it was hoped that the dimensions deter-